A New Generation of Thick-Film Gold Conductor Pastes

IMPROVED PROPERTIES OF GLASS-FREE PREPARATIONS

Good adhesion, high conductivity, ease of bonding and compatibility with other components are the characteristics of new types of gold conductor pastes for screen printing on to ceramics substrates.

Gold metallising preparations used hitherto in the fabrication of microelectronic circuits incorporate finely divided glass powder or frit. Such preparations are used extensively to produce high conductivity networks by screen printing and firing these materials on to ceramic substrates. On firing, the glass softens, diffuses through the gold film to the ceramic surface, and on cooling acts as an adhesive, binding the gold metallisation to the substrate. The applications of gold metallisations in hybrid microelectronics, where these materials offer inexpensive means for eutectic and thermocompression bonding, were reviewed recently in this journal by R. G. Finch (1).

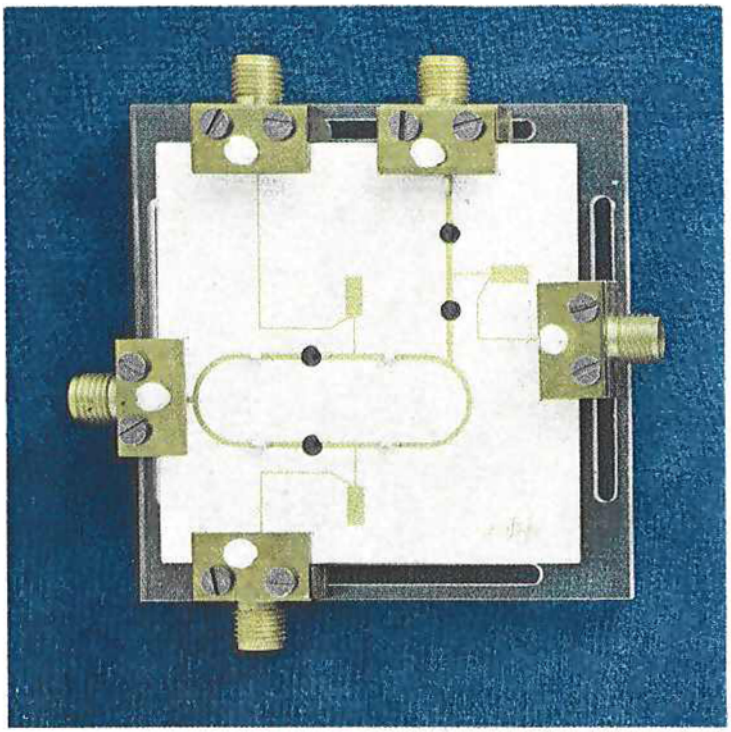
With increasing complexity and sophistication of microelectronics, however, several limitations inherent in these conventional gold conductors become apparent. The main problem is associated with the presence and distribution of the glass phase in the fired gold film. In some cases the ideal situation would be for the glass to concentrate at the ceramic-metal interface with a fairly rapid decrease in concentration of frit through the film, producing gold metallisations with an essentially glass-free surface. While this would yield suitable conditions for eutectic bonding silicon devices and for the thermocompression and ultrasonic bonding of fine wires, the presence of high concentrations of glass at the ceramic surface would provide thermal impedances hindering rapid dispersion of heat when the circuit is in operation. Unless this heat is dispersed efficiently, the life-times of some high-density microelectronic circuits would be drastically curtailed.

In practice, of course, such conditions seldom, if ever, prevail, and gold films are fabricated which have a proportion of glass residing on or very close to the free surface of the metallised layer. The presence of vitreous material in this area is accompanied by imperfect die and wire bonding acting as potential sources of trouble capable of limiting the operational times of hybrid circuits. Moreover, glass residing near the surface is not the ideal configuration of conductor films for use in microwave applications where the well-known 'skin-effect' prevails, the major part of the current being conducted by the peripheral layers of the metallisation.

To avoid these disadvantages of thick-film metallisations, the development of glass-free gold pastes has recently received a considerable amount of attention. Among the first to seek alternative methods of bonding metal films to ceramic substrates for use in microelectronic applications were R. G. Loasby, N. Davey and H. Barlow of the Microcircuit Technology Group at the U.K. Atomic Energy Authority, Aldermaston(2). Of possible methods of bonding metal to ceramic, only two were considered worthy of further examination; these were identified as, respectively, reactive metal bonding and sintered oxide layer. The well-established molybdenum-manganese process provides the best known example of the former method. Manganese fired under oxidising conditions forms a spinel $MnO\ Al_2O_3$ with alumina which is penetrated readily at elevated temperatures by molybdenum deposited at a subsequent stage. In the present context, however, this process suffers the disadvantages of high firing temperatures requiring special atmospheric environments.

The second method, sintered oxide layer, is again a two-stage process in which a metal oxide is sintered and reacted with alumina, followed by a reduction stage in which the unreacted oxide is converted to the metal. Examples of this method are given by transition metal oxides, in particular, those of cobalt, copper, nickel, and tantalum.

Clearly, the great advantage of both these approaches in present applications is that they offer a glass-free method of joining metal films to ceramic substrates, although attention was confined by Loasby and his colleagues to preparations involving silver-bearing pastes. This general line of approach has, however, been extended to encompass glass-free gold metallisations and was the subject of a paper presented at the International Microelectronics Symposium held in Washington in 1972. The authors, Baynard R. Smith and Robert L. Dietz of the Owens-Illinois Glass Company(3), showed that



The higher purity and therefore higher conductivity of the new type of glass-free gold conductor pastes, coupled with their excellent adhesion to the ceramic substrate, provide an improved means of producing conductor networks in microwave circuits. This component is designed for a proposed microwave landing system being developed by the Royal Aircraft Establishment at Farnborough. The conductor network has been screen printed and fired on to the alumina substrate using an Engelhard fritless gold preparation

high-strength, glass-free, chemical bonds could be formed between gold and alumina ceramics by introducing into the metallisation a small quantity of "reactive" material. According to these workers examples of this "reactive" material are given by the two oxides of copper. These are known to form the aluminates, $Cu(AlO_2)_2$ or $CuAlO_2$, depending on starting materials and processing conditions when either CuO or Cu_2O is heated with alumina(4). Smith and Dietz found that good adhesion was obtained from gold films containing a reactive material when air-fired from 960 to 1040°C using standard belt furnaces. Electron probe analyses revealed that the reactive material is dispersed uniformly throughout the fired film, possibly forming a homogeneous solid solution with gold, and that the penetration of this material into alumina is high.

The fired surfaces of these gold films were found to be readily bondable using the thermocompression technique, while strengths of the bonds were less sensitive to processing conditions than with those formed using glass-containing gold preparations. In general, adhesion strengths to alumina were claimed to be two to five times greater than those obtained from glass-containing pastes. Furthermore, the absence of a vitreous phase enhanced the formation of silicon-gold eutectic, facilitating device mounting in hybrid circuits.

These findings have been corroborated by further quantitative evaluations of the physical properties of fired fritless gold films. T. T. Hitch(5) at R.C.A. showed that the Owens-Illinois gold metallising paste not only contained copper, but also a relatively large proportion of cadmium, the presence of which was considered to "catalyse" the formation of copper aluminates. Hitch found that fritless gold films exhibited high conductivity and high adhesion, determined using a solderless peel test, providing the materials were processed as recommended.

Glass-free gold conductor pastes are now available commercially from Electro Oxide Corporation, an associated company of Owens-Illinois, and patent rights have been secured(6). Other workers in this area have, of course, expended considerable effort in the same direction, and by modification to the technique have also produced conductor pastes with improved printed and fired properties. Engelhard Industries, for example, have developed a glass-free gold paste which is capable of yielding films with high adhesion, high electrical conductivity and improved line definition of the printed area. Similar advantages are claimed for a preparation from Electro-Science Laboratories with a wide firing range from 900 to 1000°C.

Further confirmation of the advantages and potential usefulness of these glass-free preparations was provided at the meeting of the International Society for Hybrid Microelectronics, held recently in Boston. In a paper by Richard H. Zeien(7) of the Solid State Technology Centre, also at R.C.A., data for bond strengths of wires attached to gold films using ultrasonic or thermocompression techniques were

provided for three commercially available compositions. From topographical comparisons using scanning electron microscopy of both fritless and glass-containing gold films, Zeien agreed with previous workers that the former should display superior thermal and electrical properties and that wire-bonding characteristics using standard techniques should be improved. The validity of these conclusions was evaluated in a comprehensive test programme. Built in to this programme, which also included a study of wobble bonding of beam-lead frameworks, were assessments of the effects on strengths of bonds produced by small departures from recommended firing schedules of the gold films and in different post-firing treatments of bonded samples. Zeien showed, for example, that joint strengths of gold wires bonded either by thermocompression or by ultrasonics were not strongly dependent on the firing conditions tested, or influenced by post-bonding, long-term environmental exposures (e.g. 125°C for 500 hours). As expected, this was not found to hold true for aluminium wires ultrasonically bonded to gold, where the formation of brittle AuAl intermetallics readily accounts for the observed 25 per cent degradation in bond strength. On the other hand, wobble bonding of beam leads was found to be insensitive to the firing schedules of the gold films, and the joints showed no decrease in strength on prolonged exposure to elevated temperatures.

Compatibilities of glass-free gold metallisations with existing thick-film resistor and dielectric materials were also evaluated in this work. Thick-film resistors terminated with pre-fired gold conductors displayed spreads in as-fired values of ±10 per cent with stabilities of around 0.1 per cent under dry life-test conditions (125°C for 1,000 hours). Glass-free gold compositions were capable of being processed with crossover materials with no attendant loss in either adhesion or resolution, and the fired films showed no electrical continuity between the upper and lower electrode when spaced with this dielectric.

The improved properties of these novel materials should not only produce new areas of application for gold pastes, but also assist in removing one of the major causes of restricted life-times for thick-film circuits by increasing the yield of near-perfect bonds to metallised films on ceramic substrates. The anticipated increase in reliability of thick-film hybrid circuits will place this technology in a more favourable competitive position, capable of producing economically a wide range of microelectronic assemblies of advanced specification.

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References

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Thickness Measurement of Gold Deposits

Accurate and reliable determinations of the thickness of electrodeposited gold coatings are essential to both the electroplater and the user. The methods involved vary from spot checks by relatively simple techniques to sophisticated procedures to form the basis of statistical control of production. A great number of testing methods is now available, some direct—giving the true linear thickness of the deposit—and some indirect, measuring thickness in terms of weight of coating per unit area or through the response of the deposit to some form of external radiation.

A useful review of all the available techniques suitable for gold electrodeposits, with their individual advantages and limitations, has now been prepared by F. H. Reid and published in the first and second issues of *Circuit World*, the journal of the recently formed Association of Circuit Technologists.

The direct optical methods described include the simple procedure of determining thickness on a carefully prepared section of the coating under the microscope, the chord method in which thickness is derived from microscopic measurement on an oblique section exposed by grinding a shallow groove on the coating surface, the use of interference microscopy to measure the difference in level between unplated and plated areas, the depth of focus method, and the light profile method of measuring step height between plated and unplated areas.

The chemical and electrochemical methods reviewed include the simple strip and weigh procedure, and anodic dissolution at constant current in a test cell, the time for dissolution giving a measure of thickness.

The activation techniques, more suited to large numbers of routine measurements, include X-ray and beta-ray back scatter. While the former involves a high capital cost of equipment, the latter technique is now supported by the availability of relatively inexpensive and compact instrumentation and provides the most generally convenient non-destructive method.

The author emphasises, among other factors, the importance of both electroplater and user employing the same method of measurement, or, if this is not practicable, of tests being carried out to establish the closest correlation between the methods adopted.